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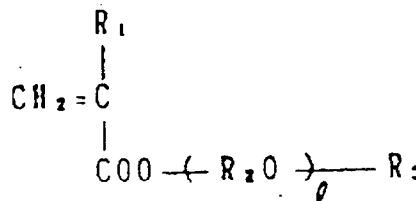
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TITLE : WASHABILITY-IMPROVING AGENT
FOR FIBER PRODUCT



ABSTRACT : PURPOSE: To improve the subject agent preventing the generation, re-adhesion, etc., of scums produced in dying processes and having excellent metal ion chelate dispersibility by using a copolymer of a specific monomer with maleic acid, acrylic acid, etc., in a specified ratio, the copolymer having a specific mol.wt.

CONSTITUTION: A washability-improving agent for fiber products comprises a copolymer of (A) a monomer of the formula (R_1 is H or methyl; R_2 is ethylene or propylene; R_3 is H, methyl, etc.; l is 1-40) with (B) a monomer selected from maleic acid, (meth)acrylic acid and salts thereof in an A/B weight ratio of 0.06-1.0 (the weights of the structural monomers), the copolymer having an average mol.wt. of 1000-10000. When the agent is added in an amount of ≥ 0.2 g/l to a bath in dying and finishing processes, the agent forms a chelate with metal ions brought into the bath to prevent the re-adhesion of the metal ions to the web, prevent the produced scums and depress the re-adhesion. In an alkali weight-reducing process, the washing of oligomers, etc., is improved to provide a good touch for the web.

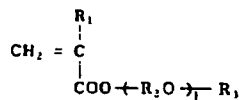
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91-278446/38 AB7.F06 (A14) NKKK 12.12.89
 NIKKA CHEM IND KK *JO 3185-184-A
 12.12.89-JP-320591 (13.08.91) C081-220/06 C081-222/02
 C11d-03/37 D06m-15/27
 Cleaning properties-improving agent for fibre prod. - is copolymer
 of methoxy:polyethylene glycol-400 methacrylate and least one of
 maleic acid, acrylic acid etc.
 C91-120947

A cleaning properties-improving agent (a) for fibre product
 is a copolymer of (A) monomer of formula (I) with (B) at
 least one monomer selected from maleic acid, acrylic acid,
 methacrylic acid and its salt in a A/B wt. ratio of 0.05-1.0
 The copolymer has an average molecular wt. of 1000-10,000



R_1 = H or CH_3 ;
 R_2 = ethylene or propylene;
 R_1 = H, CH_3 or C_2H_5 ; and
 l = integer of 1-40.

A(4-F1A, 10-E7B, 12-S5T, 12-W12C)-F(3-B, 3-B)

USES/ADVANTAGES

(a) is useful in desising, off-bleaching and
 soaping. (a) is used in a conc. of 0.05 g/l, pref. 0.2 g/l
 or more to products having a 3% solid content. (a) has
 good compatibility to nonionic surfactants and anionic
 surfactants, and good alkali resistance.

EMBODIMENT

Monomer (A) is, e.g. methoxypolyethyleneglycol # 400
 methacrylate, polyethyleneglycol # 600 methacrylate or
 polypropyleneglycol methacrylate.

EXAMPLE

140 g water was heated at 75°C in a nitrogen gas
 atmos.. To the water were dripped 150 g of a monomer soln
 which contained 76.5 g sodium acrylate, 13.5 g methoxy-
 polyethyleneglycol # 400 methacrylate and 0.1 g octyl
 thioglycolate and 0.12 g potassium persulphate dissolved in
 10 g water over 1 hr. The mixt. was polymd. at 80-85 °C
 for 2 hr. and cooled to obtain 300 g of a transparent liq.
 having a viscosity of 80 cp. (6ppW90CGDwgNo0/0).

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(54) Title of the invention A detergent properties enhancer
for fibre products

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¹ Translator's Comment: This alternative spelling frequently appears on the Internet particularly in the case of commercial product specifications.

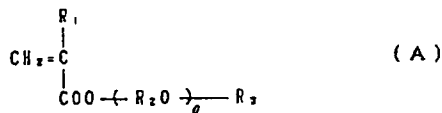
Specification

1. Title of the Invention

A detergent properties enhancer for fibre products

2. Scope of Claim

A detergent properties enhancer for fibre products which is a copolymer of (A) monomer represented by the following general formula, and at least one monomer (B) selected from maleic acid, acrylic acid, methacrylic acid and the salts of these, and the weight ratio A/B of the constituent monomers lies in the range 0.05 to 1.0, and the average molecular weight lies in the range 1,000 to 10,000.



In the above formula, R_1 represents hydrogen or methyl, R_2 represents ethylene or propylene, R_3 represents hydrogen, methyl or ethyl, and l is an integer in the range 1 to 40.

3. Detailed Description of the Invention

[Industrial Field of Application]

The present invention relates to a detergent properties enhancer for fibre products. More particularly, the present invention relates to a detergent properties enhancer for fibre products which can be used for cellulose fibres such as cotton and flax, synthetic fibres such as polyester, nylon and acrylics, and their blends, at the time of desizing, scouring, bleaching or soaping, or at the time of the mercerizing of cotton,

the alkali weight-reduction of polyester or for the cleaning of dyeing vessels, and which has good compatibility with nonionic surfactants and anionic surfactants and is outstanding in its alkali resistance.

[Prior Art]

It is known that cellulose fibres such as cotton and flax often contain heavy metal ions such as iron, calcium, copper, manganese and magnesium in the fibres, and that in desizing, scouring and bleaching processes, fibre embrittlement, pinhole generation and roller staining, etc, may be brought about.

Again, in the case of the scouring of synthetic fibres, in particular polyester, as a result of the generation of water-insoluble salts by the reaction between water and/or divalent or trivalent metal ions present in the fibre with the acrylic size or with terephthalic acid salts, or as a result of the washing-out of oligomers from within the polyester or of the titanium dioxide used as a delustrant, problems are known to arise in the scouring or in the subsequent dyeing.

In order to prevent such problems in the case of cellulose fibres there is known the use, at the time of scouring/bleaching, of a stabilizer for hydrogen peroxide bleaching in which the chief component is a poly- α -hydroxyacrylate (for example Neorate PLC-7000, produced by the Nicca Chemical Co.) as disclosed in JP-A-62-185797. In this way, the problems which arise due to the silicates normally used as stabilizers and the problems such as the generation of pinholes caused by the reaction between the aforesaid metal ions and the

hydrogen peroxide used as the bleaching agent, are prevented.

Furthermore, in order to prevent problems in the scouring of polyester, there has been employed a method for raising the detergent efficiency by jointly employing, in the cellulose fibreⁱ desizing, scouring and bleaching stages, a chelating agent such as ethylenediaminetetraacetic acid (EDTA) or diethylenetriaminepentaacetic acid (DTPA) together with a polycarboxylate such as sodium polyacrylate, sodium polymethacrylate or sodium polymaleate (JP-B-59-179681).

[Problems to be Resolved by the Invention]

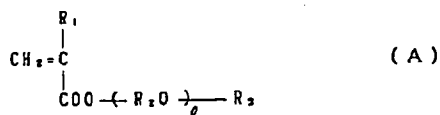
In the case of the polyphosphates such as sodium tripolyphosphate which are jointly employed at the time of desizing, scouring, bleaching or soaping, or at the time of the mercerizing of cotton, the alkali weight-reduction of polyester or the cleaning of dyeing vessels, and in the case too of the aminocarboxylate type organic chelates such as EDTA and DTPA, in the high pH region their solubility is lowered so their chelating function falls, and when the hardness of the water used exceeds a certain level, their chelating efficiency is reduced. There is also the problem of the formation of scale due to hydrolysis of polyphosphates. Hence, these materials are not very effective.

It is also known that, in the case of polycarboxylates such as sodium polyacrylate, sodium polymethacrylate or sodium polymaleate, the improvement in the detergent efficiency varies with the degree of polymerization and, in continuous treatments, variations in effect can also arise due to selective adsorption.

Furthermore, these materials have poor compatibility with nonionic surfactants and anionic surfactants, and so it has been difficult to prepare concentrated stock solutions.

[Means for Resolving the Problems]

In order to resolve the aforesaid problems, the present invention offers a detergent properties enhancer for fibre products which is a copolymer of (A) monomer represented by the following general formula and (B) at least one monomer selected from maleic acid, acrylic acid, methacrylic acid and the salts of these, and the weight ratio A/B of the constituent monomers lies in the range 0.05 to 1.0, and the average molecular weight lies in the range 1,000 to 10,000.



In the above formula, R_1 represents hydrogen or methyl, R_2 represents ethylene or propylene, R_3 represents hydrogen, methyl or ethyl, and l is an integer in the range 1 to 40.

As examples of monomer (A) which are effective in the present invention, there are methoxy polyethylene glycol "1000 methacrylateⁱⁱ, polyethylene glycol "400 methacrylate and polypropylene glycol "600 methacrylate. It is also possible to jointly employed polypropylene glycol methacrylate and polyethylene glycol methacrylate.

Monomer (B) is at least one monomer selected from maleic acid, acrylic acid, methacrylic acid and the salts of

these. The preferred salts are water-soluble salts such as the sodium, potassium, ammonium, monoethanolamine and diethanolamine salts.

The weight ratio of the constituent monomers A/B is appropriately in the range 0.05 to 1.0, and preferably in the range 0.1 to 0.5. Furthermore, an average molecular weight in the range from 1,000 to 10,000 is appropriate.

In order to obtain the aforesaid copolymer, the polymerization is carried out for example under a flow of nitrogen in the presence of a radical initiator. Useful initiators are persulphates such as potassium persulphate, sodium persulphate and ammonium persulphate, redox initiators based on a combination of a persulphate and sodium bisulphite, etc, and also hydrogen peroxide and water-soluble azo initiators. The amount of initiator is appropriately 0.05 to 1.0 part by weight per 100 parts by weight of the monomer.

An appropriate polymerization temperature and time are 50-90°C for 2 to 5 hours.

Water is employed for dissolving monomer (A) and monomer (B). In the case where there is used as monomer (B), or as a part of monomer (B), polypropylene glycol methacrylate or polypropylene glycol acrylate, it is preferred that there also be added a water-miscible solvent such as isopropyl alcohol or Butyl Cellosolve.

The joint use of a chain transfer agent such as octyl thioglycolate is effective for the purposes of adjusting the degree of polymerization.

The concentration of the detergent properties enhancer of the present invention used, based on a product of solids content 30%, should be at least 0.05 g/litre and preferably at least 0.2 g/litre.

As examples of the equipment used at the time of desizing, scouring, bleaching or soaping, in which the detergent properties enhancer of the present invention is employed, there are winch dyeing machines, jet dyeing machines, cheese dyeing machines, jig dyeing machines, washers and other types of batch equipment, and J-box, L-box, purple rangeⁱⁱⁱ, open soapers and other types of continuous equipment.

In the case where the detergent properties enhancer of the present invention is used in the mercerizing of cotton or flax, it can be employed in the mercerizing bath and/or in the soaping bath of a yarn mercerizer or mercerizer for knitted or woven material.

In the case where it is used in the alkali weight-reduction of polyester, it can be employed in a hung, pad-steam or cold-pad batch weight-reduction bath or in the soaping bath. Furthermore, as a dyeing vessel cleaner, it can be used for jet dyeing machines, beam dyeing machines, cheese dyeing machines, Overmeyer dyeing machines and the like.

[Action]

In the case of ordinary polycarboxylic acids, that is to say the homopolymers of maleic acid, acrylic acid, methacrylic acid and their salts, compatibility with nonionic surfactants and ionic surfactants is poor, and

the joint use thereof only becomes possible by dilution. This is thought to be because of poor compatibility due to the molecular weight difference between the low molecular weight surfactant and the high molecular weight polycarboxylic acid, and the difference in compositional units between the two structures.

In contrast, the detergent properties enhancer of the present invention contains a polyethylene glycol or polypropylene glycol chain in the side chains, so there is excellent compatibility with nonionic surfactants, and there is also excellent compatibility with anionic surfactants, in particular the phosphate ester salts and sulphated derivatives of alkyl aryl ether or alkyl ether type nonionic compounds.

By varying the molecular weight of the polyethylene glycol or polypropylene glycol, or the compositional ratio of the polyethylene glycol to the polypropylene glycol, it is possible to achieve mixing at high concentrations with surfactants ranging from high HLB to low HLB nonionic surfactants and with anionic surfactants.

By the joint use of the detergent properties enhancer of the present invention, there may be achieved a synergistic enhancement in the scouring and soaping effects of nonionic surfactants and anionic surfactants.

Furthermore, by the action of the copolymerized polycarboxylic acid, it is possible to prevent the generation and re-adhering of various kinds of scum produced between metal ions such as iron, copper and calcium with sizes, oils and unanchored dyestuff, and to

enhance the dispersion thereof, so that excellent results are obtained in the subsequent dyeing and finishing stages.

In the case where the detergent properties enhancer of the present invention is used in the mercerizing of cotton and flax, because of its good alkali resistance, it does not itself decompose or dissociate, so there is the effect that adhesion of scale to the rollers, etc, is prevented and the bath dispersion properties are improved.

In the case where the detergent properties enhancer of the present invention is used for the alkali weight-reduction of polyester, the detergent properties in terms of polyester oligomer, terephthalate salts and titanium dioxide, etc, are enhanced, a good handle is obtained, and level dyeing is obtained in the subsequent dyeing stage. Again, by jointly employing in the cleaning of dyeing vessels, there is the effect of enhancing the dispersion of polyester oligomer, dye complexes and various types of scum.

[Examples]

Next, the present invention is further explained by means of practical examples. However, the present invention is not to be restricted only to these practical examples.

Synthesis Example 1

140 g of water was introduced into a 500 ml four-necked flask, and warmed to 75°C under a current of nitrogen. Next, 150 g of a monomer solution in water of 76.5 g (by

conversion to solids content) of sodium acrylate, 13.5 g of methoxypolyethylene glycol "400 methacrylate and 0.1 g of octyl thioglycolate, plus an initiator solution comprising 0.12 g of potassium persulphate dissolved in 10 g of water, were added dropwise over 1 hour, and polymerization carried out for 2 hours at 80-85°C, after which the mixture was cooled and there was obtained about 300 g of a light brown transparent liquid of viscosity 80 cp (referred to below as Product 1).

Synthesis Example 2

110 g of water and 30 g of Butyl Cellosolve were introduced into a 500 ml four-necked flask, and warmed to 75°C under a current of nitrogen. Next, 150 g of a monomer solution in water of 76.5 g (by conversion to solids content) of sodium acrylate, 9.0 g of polyethylene glycol "1000 methacrylate, 4.5 g of polypropylene glycol "400 methacrylate and 0.1 g of octyl thioglycolate, plus an initiator solution comprising 0.09 g of ammonium persulphate dissolved in 10 g of water, were added dropwise over 1 hour, and polymerization carried out for 2 hours at 80-85°C, after which the mixture was cooled and there was obtained about 300 g of a light brown transparent liquid of viscosity 60 cp (referred to as Product 2).

Synthesis Example 3

15 parts (parts by weight; so too below) of a 10 mol ethylene oxide adduct of nonylphenol was added to 85 parts of Product 1, to make a total of 100 parts, and there was obtained a yellow transparent liquid of viscosity 110 cp (referred to as Product 3).

Synthesis Example 4

30 parts of the sodium salt of the phosphate ester of a 9 mol ethylene oxide adduct of nonylphenol (50% product) was added to 70 parts of Product 1, to make a total of 100 parts, and there was obtained a yellow transparent liquid of viscosity 100 cp (referred to as Product 4).

Comparative Example 1

Water was added to 30 g (by conversion to solids content) of sodium polyacrylate (molecular weight about 5,000) to give 100 g in total, and there was obtained a yellow transparent liquid of viscosity 250 cp (referred to as Comparative Product 1).

Comparative Example 2

30 g of ethylenediaminetetraacetic acid tetrasodium salt (EDTA-4Na) was made up to 100 g in total using water, and there was obtained a pale yellow transparent liquid of viscosity 8 cp (referred to as Comparative Product 2).

Performance Test Example 1

1. Compatibility with nonionic and anionic surfactants

The test sample and the surfactant were mixed together at room temperature in the following proportions, and the mixtures then left for 7 days at room temperature and at 45°C. The stability was assessed from whether or not there was precipitation or surface separation.

Mixing Ratios

	A	B	C
sample	30	50	70
surfactant	70	50	30

Results

Sample↓	Compatibility Using (i)			Compatibility Using (ii)			Compatibility Using (iii)			Compatibility Using (iv)		
	mixing ratio			mixing ratio			mixing ratio			mixing ratio		
	A	B	C	A	B	C	A	B	C	A	B	C
Product 1	O	O	O	O	O	O	O	O	O	O	O	O
Product 2	O	O	O	O	O	O	O	O	O	O	O	O
Comparative Product 1	X	X	X	X	X	X	X	X	X	X	X	X

O = stable, X = separates

(i) = nonylphenol ethylene oxide 10 mol adduct

(ii) = stearyl alcohol ethylene oxide 20 mol adduct

(iii) = sulphate of oleyl alcohol ethylene oxide 4 mol adduct (50% product)

(iv) = phosphate ester salt of nonylphenol ethylene oxide 9 mol adduct (50% product)

The products of the present invention differ from the polycarboxylate in that they show compatibility with nonionic and anionic surfactants over a broad mixing range. Hence, while the dispersing effect of the polycarboxylic acid is maintained, scouring agent and soaping agent performance is doubled.

Performance Test Example 2 (Alkali Resistance)

A bath of the following composition was left for 24 hours at room temperature, and the stability and alkali resistance determined according to whether or not there was any precipitation and surface separation.

NaOH (flakes)	x g/litre
sample	2 g/litre

Results

Sample	Amount of NaOH		
	50 g/litre	100 g/litre	200 g/litre
Product 1	O	O	O
Product 2	O	O	O
Product 3	O	O	Δ
Product 4	O	O	O
Comparative Product 1	O	O	O
Comparative Product 2	O	O	Δ

O = stable, Δ = some separation noted

Products 1 and 2 of the present invention show excellent alkali resistance in the same way as ordinary polycarboxylic acid salts. Products 3 and 4, which comprise a blend with surfactant, also show good alkali resistance due to the effects of the polyalkylene glycol methacrylate copolymer.

Performance Test Example 3 (Metal Ion Chelate Dispersion)

The following test liquid was prepared and heated for 30 minutes at 90-95%. The chelate dispersion performance was evaluated according to the state of the bath after heating, whether or not there was a residual deposit on filtering and the amount thereof.

metal ions	x ppm
NaOH (flakes)	2 g/litre
sample	1 g/litre

Results

	Ca ²⁺ 100 ppm	Fe ²⁺ 20 ppm
Product 1	O	O
Product 2	O-Δ	O
Product 3	O-Δ	O
Product 4	O-Δ	O
Comparative Product 1	O-Δ	O-Δ
Comparative Product 2	O-Δ	O-Δ
Blank	X	X

O = stable, Δ = fairly stable, x = unstable

The products of the present invention are outstanding in their metal ion chelate dispersion performance, which is a property inherent in the polycarboxylate.

Performance Test Example 4 (Effect in Enhancing the Cleaning of Dyeing Vessels)

In order to compare the dye scum (disperse dye/cationic dye complex) and polyester fibre oligomer scum dispersion properties, treatment was carried out by means of the following formulation for 45 minutes at 130°C (using a 'Mini-Color' made by Texan Giken), and then filtering carried out at 90°C, after which an evaluation was performed according to whether or not there was a deposit.

scum	0.1 g/litre
sodium hydrosulphite	2 g/litre
NaOH (flakes)	2 g/litre
sample	2 g/litre
Sunmorl DMC	1 g/litre
(Vessel cleaner made by Nicca Chemical)	

Now, no Sunmorl DMC was used in the cases where Products 3 and 4 were employed.

Results

	Scum Type	
	Dye Scum	Oligomer
Product 1	O	Δ -O
Product 2	O	Δ -O
Product 3	O	O- Δ
Product 4	O- Δ	O- Δ
Comparative Product 1	O- Δ	Δ
Comparative Product 2	Δ	Δ -X
Blank	X	X

O = no scum, Δ = slight scum, X = scum present

The products of the present invention are effective in enhancing scum dispersion, and in particular Products 3 and 4 provide a good cleaning effect without requiring any additional vessel cleaner.

Performance Test Example 5 (Scouring Effect)

Two spots of a commercial knitting oil (Pekishira A, made by Showa Shell Petroleum) were added to a cotton knitted material which had been scoured and bleached, and then this was dried for 5 minutes at 120°C, after which scouring was carried out for 5 minutes at 90°C using the formulation below.

Next, the material was introduced into a dyebath containing 0.1 g/litre of the direct dye, Kayarus Supra Blue BWL 143(produced by the Nippon Kayaku Co.), the temperature then raised and the scouring property investigated following dyeing for 5 minutes at 60°C (the scouring evaluation was based on dyeing unevenness and spotted appearance).

sample 1 g/litre

Na_2CO_3 1 g/litre
Sunmorl BH-2 0.5 g/litre
(scouring agent produced by Nicca Chemical)

Now, no Sunmorl BH-2 was used in the cases where Products 3 and 4 were employed.

Results

Sample	Scouring Property
Product 1	O-Δ
Product 2	Δ-O
Product 3	O
Product 4	Δ-O
Comparative Product 1	Δ-O
Comparative Product 2	Δ
Blank	X

O = good, Δ = normal, X = poor

The products of the present invention have a scouring enhancement effect and, in particular, Products 3 and 4 provide a good scouring effect without requiring any additional scouring agent.

[Effects of the Invention]

By employing the detergent properties enhancer of the present invention, metal components from the water employed or incorporated from the fibre are chelated, and there is also the effect that insolubilization of sizing agent, oils and ester decomposition salts by heavy metal ions is prevented.

In this way, re-deposition onto the scoured and soaped fabrics is prevented, and it is possible to prevent problems in the subsequent dyeing and finishing stages.

Furthermore, the product of the present invention has good compatibility with nonionic surfactants and anionic surfactants, so when jointly used with such surfactants there is the characteristic feature of a doubling in the performance of the surfactant.

Again, the product of the present invention resembles a surfactant in terms of structure so that it can be mixed at high concentrations with surfactants, and it is possible to produce highly concentrated mixed products of the polycarboxylic acids or polycarboxylate salts of the present invention with low molecular weight surfactants, so the practical usability is enhanced.

Translator's Notes

ⁱ Although the Japanese text does not say so specifically, presumably a polyester/cotton blend is being discussed here.

ⁱⁱ This is not explained but presumably the "1000 is the nominal molecular weight of the polyethylene glycol.

ⁱⁱⁱ The Japanese says 'paapururenji' which seems to be "purple range" but the meaning is not clear.

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